UAl2

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UAl_2: Fine structure of the f bands

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The electronic structure of the $C15$, or cubic-Laves-phase material, UAl_2 has been calculated using the linearized relativistic augmented-plane-wave method. The anomalous behavior of the electrical resistivity, specific heat, and magnetic susceptibility can be explained by the fine structure of the density of states near the Fermi energy alone, without the necessity of the introduction of drastic spin fluctuations or many-body effects.

INTRODUCTION

UAl_2 is known to possess highly anomalous electronic properties at low temperatures and in magnetic fields. The spin susceptibility χ (Refs. 1 and 2), electronic specific heat C_{el} (Refs. 3–6), and electrical resistivity ρ (Refs. 2 and 6) have very anomalous temperature dependences, which have been suggested to be due to strong spin fluctuations.[7,8] Indeed, the predictions of spin-fluctuation theory are consistent with the observed temperature dependences. Recently, however, it has been found by careful analyses of the De Haas–Van Alphen measurements that spin fluctuations play a much less important role in Pd (Ref. 9) than had been previously believed. Therefore, a more critical investigation into the electronic properties of UAl_2 is appropriate to ascertain whether the observed anomalies are due to the spin fluctuations, or whether they are due (to a greater or lesser extent) to one-electron properties arising from a complex band structure. Since these anomalies occur on a temperature scale of order 100 K (and even less), this requires the electronic band structure to be determined to within an accuracy of better than 1 mRy.

Somewhat similar anomalies in χ and NMR relaxation times are observed[10] in some $A15$ compounds, such as Nb_3Sn and V_3Si, and these have been attributed to sharp Van Hove singularities in the density of states.[11]

The sharp Van Hove singularities have been determined by band-structure calculations.[12] The anomaly in the resistivity around 100 K in these materials has received attention, yet it has not been adequately explained.[13] In the $C15$ compound UAl_2, the scale of temperature on which the anomalies are observed is somewhat finer. Thus, in order to account for them by one-electron theory, still sharper peaks in the density of states are required in order to be consistent with a single-particle explanation.

CALCULATIONS

UAl_2 crystallizes in the cubic-Laves or $C15$ structure. The space group is O_h^7 ($Fd3m$, No. 227 in the International Tables). The U atoms occupy the a positions in the face-centered-cubic unit cell; the Al atoms occupy the d positions. There are two formula units per primitive (rhombohedral) unit cell. The method used is the linearized relativistic augmented-plane-wave (LRAPW) method as described by Arko and Koelling.[14] The warped muffin-tin approximation was employed, where deviations from a constant potential in the interstitial region were included through their Fourier components, but the potential is spherically averaged inside the muffin-tin spheres. The number of LRAPW's utilized was — depending on the k point involved — 250 to 300. The convergence of the eigenvalues was determined to be of order 0.1 mRy. The doubling of the basis-set size due to the inclusion of spin-orbit coupling was avoided by using a two-variations technique. A semirelativistic set of solutions were obtained to formulate a second variational problem including spin-orbit coupling. The potential used was constructed using the overlapping charge-density model with the atomic configurations adjusted by a configuration self-consistent procedure. This procedure was found to work quite well in UAl_2 when tested against more elaborate self-consistent calcualtions. The resulting configuration for uranium with the assumed sphere radii is $7s^{1.2}6d^{1.7}5f^{2.5}$. The resulting band structure is shown in Fig. 1 along the high symmetry lines. In total, 85 independent k points were calculated in the 1/48th irreducible part of the Brillouin zone. A Fourier series consisting of 44 terms was fit to the k points calculated by the LRAPW method. The rms error of the band of most importance to this work (band 13) was 0.38 mRy (relativistic bands are much more accurately described by a Fourier series than nonrelativistic bands due to the substantially reduced number of band crossings). The density of states was calculated employing a linear interpolation scheme involving 4096 tetrahedra in 1/48th of the Brillouin zone. An energy interval of 0.1 mRy was used throughout. This density of states is shown in Fig. 2. The band structure of Fig. 1 and the density of states of Fig. 2 show a strong similarity with the electronic structure of other C15 compounds. In addition to the bands that are present in $TiBe_2$,[15] for example, there is a complex of 14 f bands between 0.05 below and 0.15 Ry above E_F. The insert of Fig. 2 shows this f band

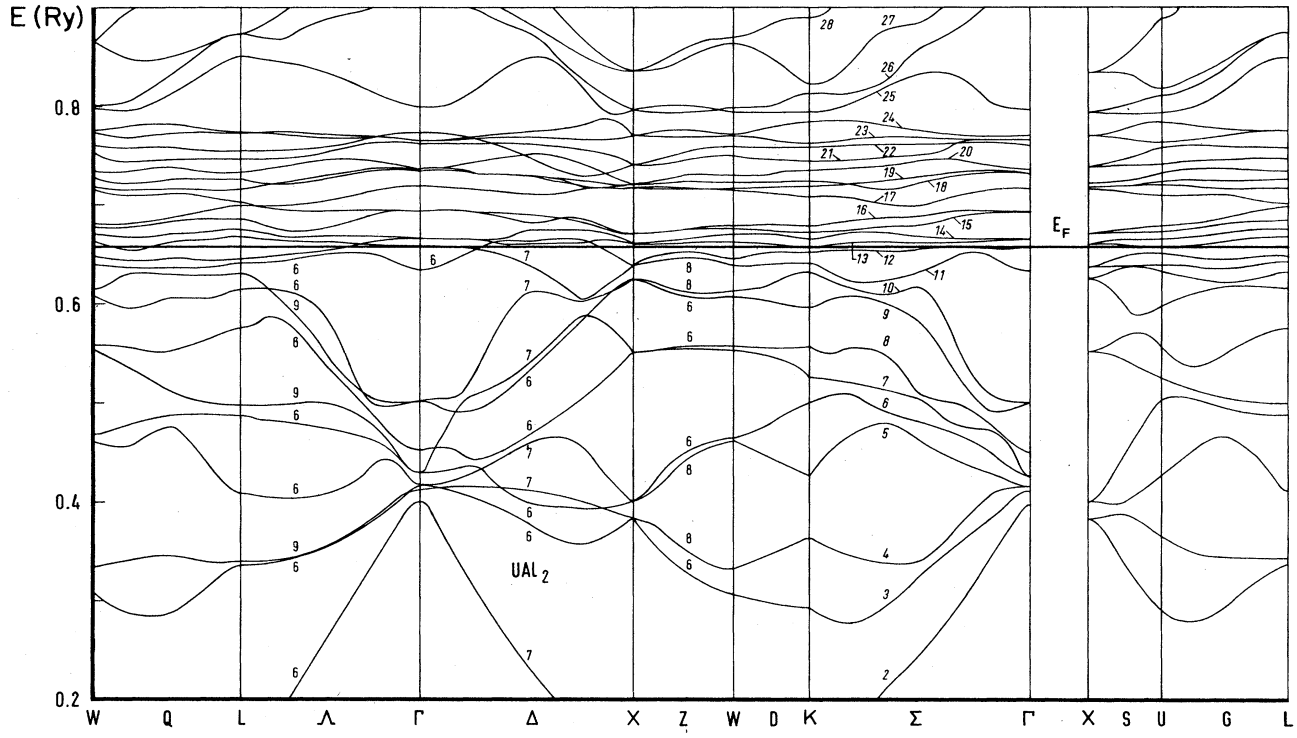

FIG. 1. The band structure of UAl_2 along the high symmetry lines of the fcc Brillouin zone.

region in more detail. The main structure in this complex is due to the spin-orbit splitting. In Fig. 3 we show the microscopic structure of the density of states of the two bands intersecting the Fermi energy (bands 12 and 13). We clearly identify the Van Hove singularity in band 13 close to the Fermi energy. Two Van Hove singularities dominate the structure at E_F, producing a near logarithmic divergence. One is of the $M1$ type, the other of $M2$. Both are close to K and U in k space. In Fig. 4 we show the band structure of the Δ line on a similar energy scale as Fig. 3. The importance of these fine structures is discussed below.

RESULTS AND DISCUSSION

From the calculated density of states, the specific heat and its temperature dependence is calculated along the lines

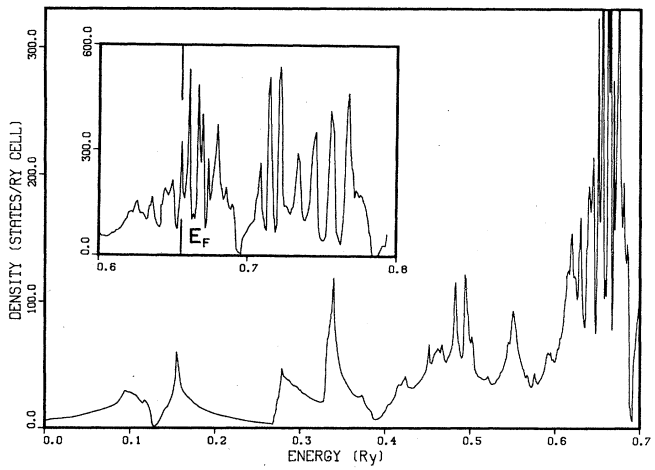

FIG. 2. The density of states (DOS) of UAl_2 as a function of energy. The insert shows the DOS of the f-band region on an expanded scale.

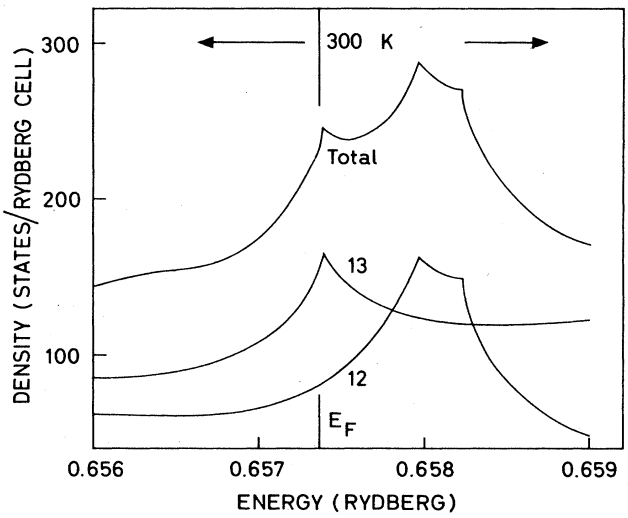

FIG. 3. The fine structure of the DOS around the Fermi energy and the decomposition into the contributions from the two bands intersecting the Fermi level.

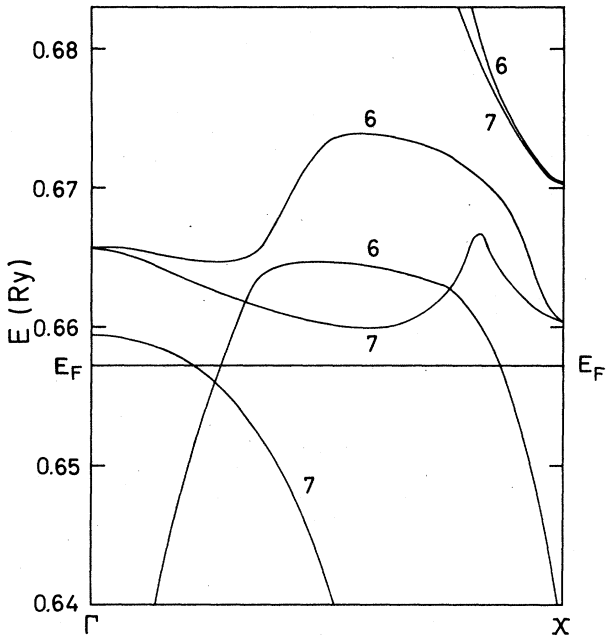

FIG. 4. The energy bands of UAl_2 along Δ on an energy scale comparable with Fig. 3.

of Overhauser and Appel.[16] Since the density-of-states curve for UAl_2 is highly nonsymmetrical around E_F, we included the shift of the Fermi level as a function of temperature. The calculated density of states at $T=0$ is 247 states/Ry cell. It decreases linearly with temperature; the decrease is 5% at 5 K, after which it saturates approximately. The enhancement of the specific heat at $T=0$ is a factor of 6.5, about twice the value of Nb. The observed temperature dependence has the same functional dependence, but up to 5 K it is four times stronger for the pure compound. The enhancement of the magnetic susceptibility over the bare Pauli value is two (ignoring any orbital contribution). Thus, an enhancement of the density of states by a factor of 2 and its energy dependence by a factor of 4 by collective effects such as spin fluctuations is sufficient to account for the experimental data. This is considerably less than assumed previously.

We will now discuss the resistivity and its temperature dependence. The calculation indicates that the electronic states are U 5-f states hybridized with more itinerant states (mainly U 6d, also U 7p, 7s and Al 3p). Within the framework of the modified tight-binding approximation these states have a moderately large electron-phonon coupling constant λ, typical of transition metals, since the width of the U 5-f band is comparable to the width of the 3-d band in transition metals, and the density of states is high. The relaxation rate h/τ equals $2\pi\lambda k_B T$ by the Hopfield relation[17] and $\rho=(m^*/ne^2)\tau^{-1}$. Since m^* is also large, the temperature dependence of ρ at low temperatures is very large, just as in Mott's s-d model.[18] When a temperature is reached where $h/t_{\mathrm{el-ph}}$ is approximately J, where $\tau_{\mathrm{el-ph}}(T)$ is the electron-phonon scattering time, and J is a typical hybridization integral, the hybridization is broken. Most of the conduction is due to the more itinerant electrons, and the temperature dependence of the resistivity decreases, because these conduction electrons possess lower values of λ and of m^*. As a result one obtains a smaller value of $d\rho/dT$. This behavior is discussed in some detail in Refs. 19 and 20.

At high temperatures, where $h/\tau_{\mathrm{el-ph}} > J$, the scattering rate of the itinerant electrons is given[20] by

$$1/\tau = 1/\tau_{sf} + 1/\tau_{ss} = J^2\tau_{ff}/h^2 + 2\pi\lambda_s k_B T/h \ ,$$

where τ_{ff} is the electron-phonon scattering time inside the sharp peak of the density of states due to the f band and λ_s is the (small) electron-phonon coupling of the itinerant electrons. τ_{ff} saturates at a value of $h/\Delta E$, where ΔE is the half-width of the peak in the electronic density of states, due to the uncertainty principle. This gives rise to a nearly temperature-independent part of the resistivity. The second term continues to increase with temperature with a small slope. What is unique about UAl_2 is that J and ΔE are particularly small, about 1 mRy. Therefore, the condition $h/\tau_{\mathrm{el-ph}}=J$ is satisfied at rather low temperatures. Specifically for $\lambda\simeq 1$, h/τ is about 4 mRy at 100 K. Inspection of the band structure indicates that there are several band crossings, or close approaches, within this energy interval from the Fermi energy. When energy levels along a high symmetry line in k space cross (such as states of types 6 and 7 symmetry in Fig. 4), then away from the symmetry line a hybridization element is allowed by symmetry, which will separate the energy levels. Inspection of the energy-level diagram of Figs. 1 and 4 indicates splittings of the order of 1, or a few, mRy. Thus, the relevant hybridization matrix elements J are of this order. It appears possible that the anomalies in the temperature dependence of the electronic properties of UAl_2 can be accounted for by one-electron theory qualitatively; the observed dependence deviates quantitatively by about a factor of 2, however.

[1]F. Y. Fradin, M. B. Brodsky, and A. J. Arko, in *Magnetism and Magnetic Materials—1972 (Denver)*, edited by C. D. Graham and J. J. Rhyne, AIP Conf. Proc. No. 10 (AIP, NewYork, 1973), p. 192.

[2]A. J. Arko, F. Y. Fradin, and M. B. Brodsky, Phys. Rev. B **8**, 4104 (1973).

[3]R. J. Trainor, M. B. Brodsky and L. Isaacs, in *Magnetism and Magnetic Materials—1974 (San Francisco)*, edited by G. H. Lander and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), p. 220.

[4]R. J. Trainor, M. B. Brodsky, and H. V. Culbert, Phys. Rev. Lett. **34**, 1019 (1975).

[5]R. J. Trainor, M. B. Brodsky, and G. S. Knapp, in *Plutonium and Other Actinides*, edited by H. Blank and R. Lindner (North-Holland, Amsterdam, 1976), p. 475.

[6]R. J. Trainor, M. B. Brodsky, and H. V. Culbert, in *Magnetism and Magnetic Materials—1976 (Joint MMM - Intermag Conference, Pittsburgh)*, edited by C. D. Graham, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 34 (AIP, New York, 1975), p. 224.

[7]M. B. Brodsky and R. J. Trainor, Physica **91B**, 271 (1977).

[8]M. B. Brodsky, Phys. Rev. B **9**, 1381 (1974).

[9]W. Joss, L. N. Hall, G. W. Crabtree, and J. J. Vuillemin, Phys. Rev. B **30**, 5637 (1984).

[10]W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Lett. **5**, 149 (1960); F. Y. Fradin and G. Cinader,

Phys. Rev. B **16**, 73 (1977).

[11]M. Weger and I. B. Goldberg, in *Solid State Physics* edited by H. Ehrenreich, F. Seitzand, and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 1.

[12]A. T. van Kessel, H. W. Myron, and F. M. Mueller, Phys. Rev. Lett. **41**, 181 (1978); T. Jarlborg, A. A. Manuel, and M. Peter, Phys. Rev. B **27**, 4210 (1983); L. F. Mattheiss and W. Weber, *ibid.* **25**, 2248 (1982).

[13]P. B. Allen, in *Superconductivity in d- and f-band Metals,* edited by H. Suhl and M. B. Maple (Academic, New York, 1980), p. 291.

[14]A. J. Arko and D. D. Koelling Phys. Rev. B **17**, 3104 (1978); G. O. Arbman and D. D. Koelling, Phys. Scr. **5**, 271 (1972); D. D. Koelling, Int. J. Quantum Chem. **85**, 473 (1974).

[15]T. Jarlborg and A. J. Freeman, Phys. Rev. B **22**, 2332 (1980); R. A. de Groot, D. D. Koelling, and F. M. Mueller, J. Phys. F **10**, L235 (1980).

[16]A. W. Overhauser and J. Appel, Phys. Rev. B **31**, 193 (1985).

[17]J. J. Hopfield, Comments Solid State Phys. **3**, 48 (1970).

[18]N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Dover, New York, 1936).

[19]M. Weger, R. A. de Groot, F. M. Mueller, and M. Kaveh, J. Phys. F **14**, L207 (1984).

[20]M. Weger and N. F. Mott, J. Phys. C **18**, L201 (1985).